DMAP (0.11 g, 0.9 mmol), and methyl 2-oxocycloheptanecarboxylate (1.0 g, 5.9 mmol) were heated to reflux in 7 mL of toluene for 30 h. Workup as described for 2. Purification by SiO_2 chromatography gave 635 mg of a colorless oil (72%) that crystallized on standing at 5 °C: $[\alpha]^{22}_{436} = 45°$ ($c = 0.28$, $CHCl_3$); mp 65.0–66.0 °C; IR (thin film) ν 2931, 2868, 1737, 1707 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75 (d, $J = 6.9$ Hz, 3 H), 0.88 (d, $J = 6.9$ Hz, 3 H), 0.91 (d, $J = 6.6$ Hz, 3 H), 0.95 (m, 1 H), 1.0 (m, 2 H), 1.4 (m, 4 H), 1.65 (m, 4 H), 1.9 (m, 4 H), 2.1 (m, 2 H), 2.6 (m, 2 H), 3.51 (dd, $J = 3.9, 10.2$ Hz, 1 H), 4.71 (ddd, $J = 4.5, 6.6, 11.1$ Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ATP 16.1 (−), 20.7 (−), 22.0 (−), 23.2, 24.4, 26.0 (−), 27.7, 27.9, 24.7, 31.3, 34.2, 40.5, 43.1, 46.8 (−), 59.0 (−), 75.0 (−), 170.1, 209.1; EIMS m/e 294 (M^+, not observed), 156 ($M^+ - C_{10}H_{18}$, 8), 138 (47), 55 (100); exact mass calcd for $C_8H_{12}O_3$ 156.0786, found 156.0786.

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Supplementary Material Available: NMR spectra of 4 (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Synthesis and Characteristics of Bis(5-carbomethoxy-4-(methylthio)-3-phenyl-2-thiazolinylidene)

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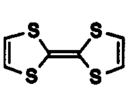
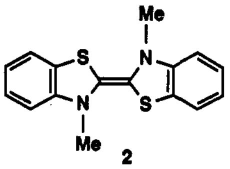
The chemistry of tetrathiafulvalene (TTF, 1) and its derivatives has been studied intensely for more than 15 years,[1] in view of their utility as starting materials for conducting organic metals. By replacing two of the sulfur atoms in a TTF moiety by nitrogen, one can change the electron density of the molecule and considerably increase its donor ability. Although the first compound of this series, the benzannelated derivative 2, was reported in 1964 by Metzger and co-workers,[2] little progress in the synthesis of other such compounds has been achieved to date.



1



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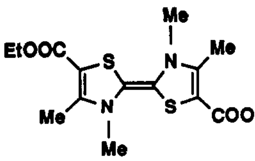

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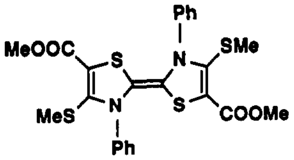
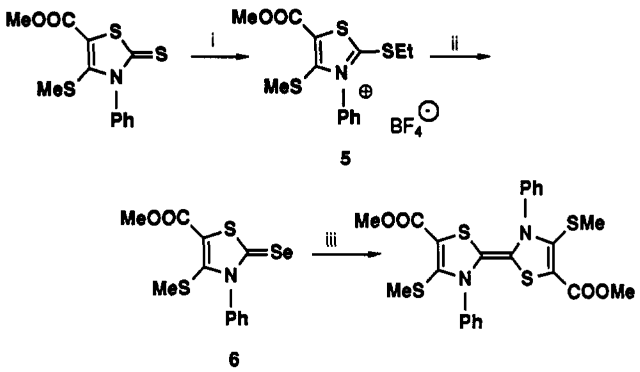


4

Bordwell and Satish recently detected several simple alkyl-substituted bis(thiazolinylidines) electrochemically, but an attempt to isolate one of these led only to oxidation products.[3] Similarly, Thummel et al. observed the two-electron electrochemical reduction of a bridged 2,2′-bithiazolium salt, but a stable reduction product was not obtained.[4] The only compound of this type heretofore reported is the diester 3, isolated by Doughty as an oxygen-sensitive, light red oil.[5]

Scheme I^a



^{a}(i) $HC(OEt)_3$, $Et_2O{\cdot}BF_3$, $CHCl_3$, 100%; (ii) NaHSe, EtOH, 85%; (iii) $P(OMe_3)$, 100 °C, 100%.

In this paper, we report the synthesis and some properties of the first noncondensed crystalline bis(thiazolinylidine) 4. In view of the expected ease of oxidation of such a compound, we chose a synthetic approach different from that employed by Metzger[2] and explored by others (Scheme I).[3,5] Our synthetic route is illustrated in Scheme I. The title compound was prepared in the last step in a quantitative yield.

The synthesis and properties of the starting 1,3-thiazoline-2-thione have been reported by us recently.[6] Conversion to the 2-(alkylthio)-1,3-thiazolium salt 5 and to the corresponding selone 6 in 85% overall yield was carried out by analogy with procedures employed in the 1,3-dithiole series.[7]

The cyclic voltammogram of 4 measured in dichloroethane solution shows two reversible peaks at 0.00 and 0.48 V in accord with the redox system shown in Scheme II.

Dication 7 was isolated as its diperchlorate by treatment of the neutral form 4 with phenyliodoso diacetate in the presence of perchloric acid in dioxane (Scheme III). The cyclic voltammogram obtained for the salt 7 is identical to that of 4 under the same conditions.

The mass spectral data obtained for the dimer 4 are in good agreement with the expected structure, the most prominent peaks being the molecular ion (84%) and the base peak corresponding to the loss of one phenyl group.

The ^{1}H NMR data obtained in $CDCl_3$ solution for the dimer 4 shows, besides phenyl protons in the region 7.51–7.28 ppm, two methyl singlets at δ 2.12 and 2.19 (SMe) and two others at 3.79 and 3.83 (OMe) ppm in ratios of 1:1. Although for the dimer 2 the E configuration was assumed,[2,3] our results testify to the existence of both E and Z isomers in $CDCl_3$ solution. The doubling of the

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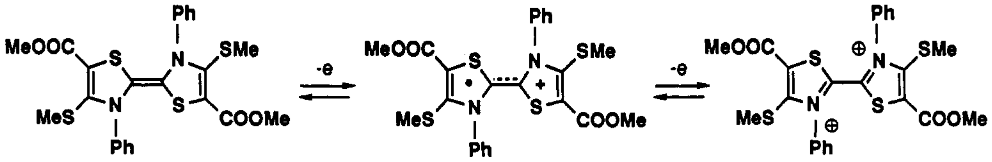
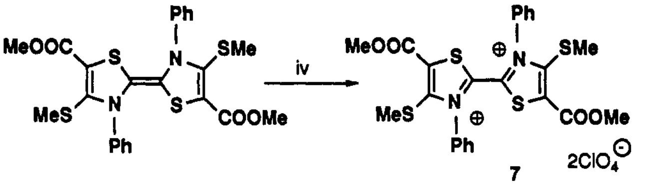
J. Org. Chem. 1992, *57*, 1009–1012

Scheme II



Scheme III[a]



7

[a] (iv) PhI(OOCMe)$_2$, HClO$_4$, dioxane, 61%.

methyl groups disappears for the dication salt 7 in CDCl$_3$ solution. The existence of 4 as an *E*/*Z* mixture is not unique among tetrathiafulvalene analogues. Thus, *sym*-diselenadithiafulvalene exists in solution as an almost equal mixture of *E* and *Z* isomers.[8]

The observed properties of compound 4 strongly suggest that bis(thiazolinylidenes) bearing appropriate electron-withdrawing groups may function as a new class of donors in the synthesis of conducting charge-transfer salts. This possibility is under investigation in our laboratories.[9]

Experimental Section

General. Cyclic voltammograms were measured in dichloroethane solution (with 0.1 M TBAHFP supporting electrolyte) with a BAS CV-27 cyclic voltammograph, platinum disk (working), platinum wire (auxiliary), and SCE (reference) electrodes. Scan rate was 0.070 V/s.

5-Carbomethoxy-4-(methylthio)-3-phenylthiazoline-2-selone (6). To a solution of 4-(methylthio)-3-phenyl-2-thioxo-1,3-thiazoline-5-carboxylic acid methyl ester (1.00 g, 3 mmol) in 15 mL of CHCl$_3$ were added HC(OEt)$_3$ (2 mL) and Et$_2$OBF$_3$ (2 mL). The reaction mixture was heated to boling and left overnight. The resulting 2-(ethylthio)-1,3-thiazolium fluoroborate was precipitated with ether, filtered off, dried, and dissolved in 15 mL of dry acetonitrile. This solution was added dropwise to a solution of sodium hydroselenide made from powdered selenium (0.53 g, 6 mmol) and sodium borohydride (0.25 g, 6.6 mmol) in 30 mL of absolute ethanol under nitrogen. After stirring for 20 min, the reaction mixture was diluted with water (100 mL). The precipitate was filtered off and washed with water. The resulting yellow solid was dissolved in benzene, and the solution was dried over CaCl$_2$ overnight then filtered through silica gel, eluting with benzene (6 × 40 mL). After removal of the solvent yellow crystals of selone 6 (1.05 g, 91%), mp 172 °C, were obtained: UV, λ_{max} ($\log_{10} \epsilon$), EtOH 327 (3.88), 380 (4.08) nm. Anal. Calcd for C$_{12}$H$_{11}$O$_2$NS$_2$Se: N, 4.07; S, 18.62. Found: N, 4.05; S, 18.75.

Bis(5-carbomethoxy-4-(methylthio)-3-phenyl-2-thiazolinylidene) (4). Selone 6 (1.5 g, 4.36 mmol) was suspended in triethyl phosphite (2.25 mL, 13.08 mmol), and the mixture was heated for 10 min at 100 °C. After the mixture was cooled to rt 10 mL of methanol was added, and the precipitate was filtered off, washed with methanol, and dried to give deep violet crystals of 4 (1.15 g, 100%): mp 254 °C; ^{1}H NMR (CDCl$_3$) δ 7.51–7.28 (m, 10 H, Ph), 3.83 and 3.79 (s, 6 H, OMe), 2.19 and 2.12 (s, 6 H, SMe); MS *m*/*e* 530 (M$^+$, 84), 453 (100), 291 (28), 265 (7), 150 (9), 135 (22). Anal. Calcd for C$_{24}$H$_{22}$N$_2$O$_4$S$_4$: C, 54.32; H, 4.18; N, 5.28; S, 24.16. Found: C, 53.88; H, 4.09; N, 5.27; S, 24.08.

Acknowledgment. We thank the National Science Foundation for partial support of this work through Grant No. CHE9001714 and IREX (International Research and Exchanges Board) for fellowship support to G.V.T.

Registry No. 4, 137627-27-1; 5, 137627-29-3; 6, 137627-30-6; 4-(methylthio)-3-phenyl-2-thioxo-1,3-thiazoline-5-carboxylic acid methyl ester, 125011-68-9.

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[9] For the sake of simplicity, we suggest the trivial name dithiadiazafulvalene (DTDAF) for 2,2′-bis(thiazolinylidene). Compound 4 would then be 3,3-diphenyl-4,4-bis(methylthio)-5,5-dicarbomethoxy-DTDAF.

2-Methoxyprop-2-yl Hydroperoxide: A Convenient Reagent for the Synthesis of Hydroperoxides and Peracids

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During the course of studies into hydroperoxide synthesis, we became interested in the nucleophilic introduction of the hydroperoxide group onto an aliphatic backbone. Standard methods for nucleophilic introduction of hydroperoxides require prolonged reaction with concentrated solutions of hydrogen peroxide under strongly basic conditions.[1,2] Based on our earlier results with ketalized hydroperoxides, we reasoned that a half-ketalized hydrogen peroxide such as 1 might rapidly react with alkyl halides under mild conditions to directly afford a protected alkyl hydroperoxide; subsequent unmasking would then cleanly provide the desired alkyl hydroperoxide[3] (Scheme I). We report herein the successful application of this strategy toward the synthesis of aliphatic hydroperoxides and a variety of peracids.

The necessary reagent, 2-methoxyprop-2-yl hydroperoxide (1), is easily generated through ozonolysis of 2,3-dimethylbutene in either MeOH or MeOH/CH$_2$Cl$_2$.[4] Removal of solvent in vacuo and replacement with the desired reaction solvent affords easily handled solutions of 1.[5] The application of 1 to the synthesis of aliphatic perketals and hydroperoxides is shown in Scheme II. Reaction of 1, an alkyl halide, and CsOH in DMF results in rapid disappearance of the halide and formation of the corresponding perketal.[6] Reactions with primary bromides proceed cleanly to afford moderate to good yields of the corresponding perketals. All perketals are stable to

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[5] We have always limited preparation of 1 to ≤3 g. Peroxides and hydroperoxides are handled and stored at or below room temperature in the presence of 0.1% butylated hydroxytoluene (BHT).

[6] The calculated amounts of 1 are based upon the quantity of dimethylbutene initially subjected to ozonolysis. A requirement for a slight excess of 1 is likely due to loss of material during concentration.